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A METHOD FOR THE DETERMINATION OF Cr, Mn, Mo, Ni, AND B IN LOW ALLOY STEEL ARMOR USING ATOMIC ABSORPTION SPEC-TROSCOPY AND INDUCTIVELY COUPLED ARGON PLASMA EMISSION SPECTROSCOPY

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MATERIALS TESTING AND EVALUATION BRANCH

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ABSTRACT

A more reliable, accurate, and rapid method to determine the concentration of Cr, Mn, Mo, Ni, and B in low alloy steel armors is described. The various procedures of sample dissolution by acids are given. For each element, the high and low intensity spectral lines are determined for the analytical ranges of interest. Analytical results using spiked standards and standard reference materials from the National Institute of Standards and Technology are in agreement with the certified values.

INTRODUCTION

The strength and resistance of an armor steel to ballistic impact can be strongly dependent on the microstructure as well as the alloying elements. Armor steels currently used by the Army consist of a variety of low alloy steels. The composition of Cr, Mo, Ni, Mn, B, and other alloying elements may vary over a wide concentration range depending upon manufacturers and the military specifications. Consequently, accurate and precise knowledge of chemical composition is a valuable asset in the research and development of armor steels.

There are many analytical methods available to determine the chemical composition of armor steels. Some have high accuracy but the procedures are tedious and complicated, such as those employing classical wet chemistry, and traditional atomic absorption spectrophotometry with multi-dilution steps. The fast but less accurate methods are arc-spark optical emission, X-ray fluorescence, and inductively coupled argon plasma emission spectrometry. These rapid methods often require extensive sample preparation. To minimize interference and analytical errors, the specimen must also be made identical to the standard in size, shape, surface uniformity, composition, and matrix. The purpose of this study is to develop a simple analytical procedure that yields the high accuracy of atomic absorption spectrophotometry (AA) and the speed of inductively coupled argon plasma emission spectrometry (ICP), using a minimum of analytical steps in sample preparation, dilution, and wet chemical procedures.

PROCEDURE

Background

A literature search was conducted to determine whether any previous work had been accomplished in which AA and ICP were used conjunctively, for the rapid and accurate analysis of the subject elements in armor steel. Literature showed only general and specific procedures using the most sensitive wavelengths and optimum instrumental operating conditions for each element of interest.

Other standard methods were also examined. They included classical wet methods and ASTM standard methods (E-30 and E-350); arc-spark optical emission and X-ray fluorescence spectrometry.

Acid dissolutions of steel specimen were experimented with in the laboratory. They included HCl, HNO_3, H_2SO_4, H_3PO_4, H_2SO_4/H_3PO_4, ranging from 10% to 50% by volume. No $HClO_4$ was used due to the inherent danger and laboratory safety requirements involved. The most desirable dissolution techniques were found to be applications of diluted HCl (1:1) with HNO_3 drops, and the 15% H_2SO_4/15% H_3PO_4 mixture. The diluted HCl/HNO_3 drops dissolution technique was chosen as the most desirable. It was easy to use, less hazardous, and did not have the viscosity problem associated with H_2SO_4.

The effect of acid types and concentrations was also investigated. Different acid and solution viscosity affect aspiration rates and results. The best specimen solutions were found to be those containing ≤ 10% HCl by volume.

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Experiment

Equipment

A Perkins-Elmer Model 5100 atomic absorption spectrophotometer and a Jarrell-Ash Model 955 Plasmacomp emission spectrometer were utilized for this project. The operating procedures were described by the manufacturers and will not be repeated.

Specimen Preparations

- Weigh out 0.5 g of steel chips and placed into a 250 ml beaker. Slowly add 30 ml 1:1 HCl, cover and heat on hot plate at medium heat (do not boil) until reaction subsides and metal is dissolved. Slowly add 2 ml HNO_3 dropwise to oxidize the carbon, heat until nitrous oxide fume is expelled. Remove from heat. Upon cooling, pour solution into a 250 ml volumetric flask, rinse beaker with distilled water and add to the flask. Bring solution to volume with distilled water, shake or mix well. (This is Solution A.)

- Pipet 10 ml from Solution A, bring up to volume in a 100 ml volumetric flask with addition of 1 ml HCl to keep the solution stable. (This is Solution B.)

- The 250 ml volumetric flask (Solution A) is to be analyzed by ICP.

- The 100 ml volumetric flask (Solution B) is to be analyzed by AA.

Preparation of Standard Stock Solutions and Calibrating Standards

- All chemicals are of high purity, "spec pure" grade or better.

  Standard stock solutions = 1000 ug/ml.

  Chromium. Dissolve 2.844 g of potassium dichromate $(K_2Cr_2O_7)$ in distilled water and dilute the solution to 1 liter.

  Manganese. Dissolve 1.000 g of powdered manganese. metal in 20 ml of HNO_3. Dilute the solution to 1 liter with 1% HCl.

  Molybdenum. Dissolve 1.000 g of powdered molybdenum metal in 20 ml of HNO_3. Dilute the solution to 1 liter with 1% HNO_3.

  Nickel. Dissolve 1.000 g of powdered nickel metal in a minimum amount of 1:1 HNO_3. Heat the solution slowly to effect dissolution, cool, and dilute to 1 liter with 1% HNO_3.

  Boron. Dissolve 5.72 g of boric acid (H_3BO_3) in distilled water and dilute the solution to 1 liter, store solution in a polyethylene bottle.

- Preparation of Calibrating Standard

  Dissolve 0.475 g electrolytic iron [National Institue of Standards and Technology (NIST) Standard Reference Materials (SRM) 365] using the same method as described in the specimen preparation section. Add the appropriate volumes of standard stock solutions and HCl before bringing up to volume with distilled water. Table 1 lists the standards for iron and alloy elements.

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Table 1. STANDARDS FOR IRON AND ALLOY ELEMENTS

Element	Solution		Equivalent Weight in Steel
Fe	2000 ug/ml	=	100.00%
	1900 ug/ml	=	95.00%
Cr	50 ug/ml	=	2.50%
	20 ug/ml	=	1.00%
Mn	50 ug/ml	=	2.50%
	20 ug/ml	=	1.00%
Mo	20 ug/ml	=	1.00%
Ni	100 ug/ml	=	5.00%
	50 ug/ml	=	2.50%
B	1 ug/ml	=	0.05%

Experimental Procedure

For each element several wavelengths were studied using the spiked stock and standard solutions to obtain the optimum wavelengths and linearity for the specific concentration ranges in the armor steels under investigation. The elements of interest and ranges of concentration are listed in Tables 2 and 3. These were the most common ranges encountered within the analytical chemistry laboratory at the U.S. Army Materials Technology Laboratory (MTL).

Table 2. LOW ALLOY STEELS
PERCENT MAXIMUM LIMIT

Cr	0 - 2.5%
Mn	0 - 2.5%
Mo	0 - 1.0%
Ni	0 - 2.5%

Table 3. (AISI 4340)

Cr	0.70 - 0.90%
Mn	0.60 - 0.80%
Mo	0.20 - 0.30%
Ni	1.65 - 2.00%

The selected wavelengths, slit (band width), linearity, sensitivity checks, and element concentration ranges are listed in Table 4 for AA. The wavelength, linearity, and element concentratir anges are liste. in Table 5 for IC?.

Steel standards from the NIST were analyzed as a comparison to determine the accuracy and precision of the method. The average of six measurements for each element is listed in Tables 6 and 7 along with the NIST certified values for SRM 361, 362, 363, and 364.

Table 4. AA ANALYSIS OF ARMOR STEEL COMPARISON OF SENSITIVE AND
LESS SENSITIVE SPECTRAL LINES

	Range Wavelength (nm)	Slit* (nm)	Linearity (ug/ml)	Sensitivity Check* At 0.2 Absorbance (ug/ml)	Analytical Conc. % Max. Solution B
Cr	357.90†	0.7	5	4.0	0 - 2.5%
	429.00	0.7	5	20.0	- 12.5%
	427.50‡	0.7	7	15.0	- 7.5%
Mn	279.50†	0.2	2	2.5	0 - 1.0%
	279.80	0.2	5	3.0	2.5%
	403.10‡	0.2	80	25.0	- 12.5%
Mo	313.30	0.7	40	30.0	- 2.0% as is
	319.40‡	0.7	60	65.0	- 3.0% no dil.
Ni	232.00†	0.2	2	7.0	0 - 1.0%
	341.50	0.2	10	20.0	- 5.0%
	346.20	0.2	20	40.0	- 10.0%
	352.50‡	0.2	20	20.0	- 10.0%
B	249.72◊	0.7	400	600.0	Insensitive to
	208.90	0.2	—	1200.0	our samples

NOTE: Nitrous oxide-acetylene flame is recommended for Cr, Mo.
Air-acetylene flame is recommended for Mn and Ni.
*Perkin-Elmer, Analytical Methods for AA Spectrophotometry, (1982).
†Best wavelengths for diluted solutions.
‡Wavelengths for more concentrated solutions.
 (The burner head system must be cleaned frequently to prevent clogging.)
◊ Atomic absorption is not sensitive enough for trace boron analysis.
 Boron is a refractory element.

Table 5. ICP ANALYSIS OF ARMOR STEEL COMPARISON OF SENSITIVE
AND NON-SENSITIVE SPECTRAL LINES

	Wavelength (nm)	Linearity (ug/ml)	Analytical Range (ug/ml) Solution A	Analytical Range Conc. % Max. Solution A
Cr	267.7	300	40.00	2.00%
	298.9	300 - 450	40.00 - 60.00	2.00 - 3.00%
Mn	348.2	300	100.00	5.00%
Mo	202.2	300	40.00	2.00%
	263.8	300 - 1500	40.00 - 200.00	2.00 - 10.00%
Ni	243.7	1000	40.00 - 500.00	2.00 - 25.00%
	231.6	40	40.00	2.00%
B	249.7	100	0.01 - 0.02	0.0005 - 0.01%

NOTE: A larger specimen should be used for the accurate determination
o' ʰoron with this technique

Table 6. AA RESULTS OF ARMOR STEEL (CERTIFIED AND EXPERIMENTAL VALUES)

Element	Cr	Mn	Mo	Ni
NIST SRM 361				
Certified Value	0.690	0.660	0.190	2.000
AA Value	0.690	0.660	0.170	2.010
Deviation	0.000	0.000	0.020	0.010
Range	0.680 - 0.700	0.650 - 0.670	0.150 - 0.190	2.000 - 2.020
NIST SRM 362				
Certified Value	0.300	1.040	0.680	0.590
AA Value	0.310	1.060	0.650	0.600
Deviation	0.010	0.020	0.030	0.010
Range	0.300 - 0.320	1.040 - 1.080	0.620 - 0.680	0.590 - 0.610
NIST SRM 363				
Certified Value	1.310	1.500	0.028	0.300
AA Value	1.330	1.530	0.022	0.310
Deviation	0.020	0.030	0.006	0.010
Range	1.310 - 1.350	1.500 - 1.560	0.016 - 0.028	0.300 - 0.320
NIST SRM 364				
Certified Value	0.063	0.255	0.490	0.144
AA Value	0.070	0.266	0.440	0.140
Deviation	0.007	0.011	0.050	0.004
Range	0.063 - 0.077	0.255 - 0.277	0.390 - 0.490	0.136 - 0.144

NOTE: Values expressed in weight percent.
Average of six results on each element.

Table 7. ICP RESULTS IN WEIGHT PERCENT
(CERTIFIED AND EXPERIMENTAL VALUES)

Element	Cr	Mn	Mo	Ni	B
NIST SRM 361					
Certified Value	0.690	0.660	0.190	2.000	0.0005
ICP Value	0.710	0.690	0.210	2.040	0.0009
Deviation	0.020	0.030	0.020	0.040	0.0004
Range	0.690 - 0.730	0.660 - 0.720	0.190 - 0.230	2.000 - 2.080	0.0005 - 0.0013
NIST SRM 362					
Certified Value	0.300	1.040	0.068	0.590	0.0025
ICP Value	0.310 - 0.370	1.100	0.070	0.620	0.0054
Deviation	0.010	0.060	0.002	0.030	0.0029
Range	0.300 - 0.320	1.040 - 1.160	0.068 - 0.072	0.590 - 0.650	0.0025 - 0.0068
NIST SRM 363					
Certified Value	1.310	1.500	0.028	0.300	0.0009
ICPValue	1.340	1.550	0.030	0.330	0.0017
Deviation	0.030	0.050	0.002	0.030	0.0008
Range	1.310 - 1.370	1.500 - 1.550	0.028 - 0.032	0.300 - 0.360	0.0008 - 0.0026
NIST SRM 364					
Certified Value	0.063	0.255	0.490	0.144	0.0110
ICP Value	0.067	0.262	0.530	0.151	0.0120
Deviation	0.004	0.007	0.040	0.007	0.0010
Range	0.063 - 0.071	0.255 - 0.269	0.490 - 0.570	0.144 - 0.158	0.0110 - 0.0130

NOTE: Values expressed in weight percent.
Average of six results on each element.

RESULTS AND DISCUSSION

The results obtained by AA and ICP are tabulated in Tables 6 and 7. The data obtained by AA analyses (see Table 6) are not significantly different from those obtained by ICP (see Table 7). The discrepancies between data from the two instrumental techniques and the certified SRM values from NIST are not significantly different. In general, the ICP data deviates from the NIST certified values slightly more than those obtained by AA. The deviations were probably caused by spectral interference, plasma instability, and instrument background noise. The ICP technique was found to be more accurate but less precise than AA. The ICP technique has the advantage of speed as well as a wide linear dynamic range and a better detection limit. Moreover, this technique required less dilutions.

In steel analysis, the major drawbacks for ICP were the spectral interference problems. Matrix matching techniques using the same types and amounts of acids and similar concentrations of alloy elements in the standard solutions as was performed in this experiment minimized and compensated for the interference problems.

As indicated by this experiment, the ICP results, in general, deviated from the certified NIST SRM values slightly more than those obtained by AA. Unless absolute accuracy and precision are required, ICP is the method of choice for the routine analyses of low alloy armor steels.

CONCLUSIONS

The specimens of armor steels are readily dissolved in the acids and acid mixtures under the present investigation. The steel dissolution involving diluted hydrochloric acid (1:1) with the addition of nitric acid is considered the simplest and safest procedure. The perchloric acid dissolution is not recommended due to its inherent danger and special laboratory safety requirements.

The present method is simple, direct, and requires no pre-concentration or separations. After the acid dissolution, the sample solution is brought to volume for instrumental analysis following the minimal analytical steps. This technique eliminates a major source of analytical error, derived from the multi-step dilutions. The solution is then analyzed by a combination of these two techniques. ICP is required for Boron, a refractory element.

The data from this investigation indicates that the present method is accurate and suitable for use in Army laboratories for the analysis of low alloy armor steels.

No significant differences were found between the experimental results and those established by NIST.

RECOMMENDATIONS

The procedure described is accurate and easy to use and should be adopted by the Army laboratories in the extensive chemical analysis of low alloy armor steels.

Further studies should be made toward the modification of this method to include other elements in the armor steels such as Cu, V, Ti, Al, as well as the statistical analysis of this method.

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